

Invited

XPS Studies on Oxidation of Si

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The chemical structures of SiO_2/Si interfaces formed on atomically flat hydrogen-terminated silicon surfaces were studied. Before the formation of interface, the oxidation on hydrogen-terminated $\text{Si}(111)-1 \times 1$ and $\text{Si}(100)-2 \times 1$ surfaces does not proceed uniformly. After the formation of interface, the oxidation on these two surfaces proceeds differently. On $\text{Si}(111)$ surface the periodic changes in the interface structure appear with the progress of oxidation, which is a direct evidence of oxidation reaction at the interface, and the oxidation proceeds layer by layer, while on $\text{Si}(100)$ surface the oxidation does not proceed uniformly.

1. INTRODUCTION

Recently the following results important for the control of oxidation reaction in atomic scale have been obtained for hydrogen-terminated Si surfaces: (1) If the Si surface is terminated with hydrogen, the formation of native oxide can be suppressed,¹⁾ (2) An atomically flat H-terminated $\text{Si}(111)$ surface can be obtained by the treatment²⁾ in 40% NH_4F solution or that³⁾ in boiling water, (3) An atomically flat H-terminated $\text{Si}(100)$ surface can be obtained by annealing in hydrogen with pressure higher than 0.2 Torr at 700°C ,⁴⁾ (4) If H-terminated Si surface can be oxidized without breaking Si-H bonds, the structure of Si surface must be roughly preserved. However, the oxidation of H-terminated $\text{Si}(111)$ surface proceeds non-uniformly at 300°C in dry oxygen,^{5,6)} (5) 0.4 nm thick oxide film formed on $\text{Si}(100)$ surface at 300°C in dry oxygen, which is called preoxide in the following, is stable in ultra-dry argon even at 900°C .⁷⁾ Therefore, Si surface is stabilized by the preoxide. Through 0.5 nm thick preoxide formed at 300°C the periodic changes in $\text{SiO}_2/\text{Si}(111)$ interface structures appear with the progress of oxidation at 800°C in dry oxygen.⁸⁾ This can be correlated with layer by layer growth of oxide on $\text{Si}(111)$ surface produced by the exposure at room temperature to 2.5×10^{-7} Torr H_2O ,⁹⁾ (6) Nearly ideal tunneling transport was confirmed for ultra-thin SiO_2 grown on well-defined H-terminated $\text{Si}(100)$ surface.¹⁰⁾ The difference in surface morphology as characterized by ATR is not directly correlated with the tunneling current,¹⁰⁾ (7) Monoatomic

steps on $\text{Si}(111)$ surface do not move with the formation of native oxides,¹¹⁾ (8) It was found for the oxidation of clean $\text{Si}(100)$ surface that the chemical structures of the ultra-thin oxide films are affected by the initial surface microroughness.¹²⁾ This is not true for H-terminated $\text{Si}(100)$ surface.¹³⁾

In the following the initial stage of SiO_2/Si interface formation and the oxidation reaction at the interface during the subsequent oxidation are discussed.

2. INITIAL STAGE OF INTERFACE FORMATION

The oxidation process⁵⁾ on H-terminated $\text{Si}(111)-1 \times 1$ surfaces at 300°C in dry oxygen with a pressure of 1 Torr up to the thickness of 0.5 nm are simulated as follows⁶⁾: The amounts of intermediate oxidation states as a function of number of bridging oxygen atoms are calculated from the analysis of oxidation induced change in Si 2p photoelectron spectra. The three dimensional silicon lattice consisting of 40 atoms x 40 atoms in each layer on (111) plane is used for the simulation of oxidation. The bonding probability of silicon atom with oxygen atom is adjusted until the simulated results are almost close to the experimental results. Then, Si atom bonded with oxygen atom is found to have higher bonding probability with oxygen atoms as compared with other Si atoms. Furthermore, once the bridging oxygen atoms are produced the oxidation is found to proceed in lateral direction around these oxygen atoms. In other words the oxidation proceeds layer by layer in atomic scale.

3. OXIDATION REACTION AT THE INTERFACE

Through 0.5 nm thick oxide formed at 300°C in dry oxygen with a pressure of 1 Torr the oxidation was performed at temperatures in the range from 600°C to 900°C in the same oxidation atmosphere up to the thickness of nearly 2.0 nm. The changes in chemical structures with the progress of oxidation were studied from the measurement of Si 2p photoelectron spectra at photoelectron take off angle of 15 degrees using an ESCA-300 manufactured by Scienta Instruments AB,¹⁴⁾ which has high sensitivity, high energy resolution, and small acceptance angle for photoelectrons. Figure 1 shows typical Si 2p_{3/2} spectra with oxide film thickness as a parameter. Here, the spectral intensities of Si substrate are adjusted to be equal to each other so that it is possible to see the oxidation induced changes in interface structures, because the ratio of photoelectrons originating from intermediate oxidation states to those from Si substrate is not affected by the inelastic scattering in the oxide if the intermediate oxidation states are all localized at the interface. The dashed lines on each figure shows the average of amounts of Si¹⁺ and Si³⁺ in the thickness range from 0.6 to 1.7 nm. According to this figure, the amounts of Si¹⁺ and Si³⁺ are almost the same for two thicknesses of 0.9 and 1.7 nm. This implies that the periodic changes in the interface structures appear with the progress of thermal oxidation.

Fig. 2(a) shows the spectral intensity of Si⁴⁺ and the total spectral intensity of intermediate oxidation states as a function of oxide film thickness. The oxide film thickness on the horizontal scale in Fig. 2(a) are calculated from the analysis of Si 2p photoelectron spectra. According to Fig. 2(a), the total spectral intensity of intermediate oxidation states saturate at the oxide film thickness of nearly 0.5 nm, while the spectral intensity of Si⁴⁺ does not saturates at this thickness. Furthermore, the total spectral intensity of intermediate oxidation states agrees well with that calculated for an abrupt interface, which is shown by the dashed line in Fig. 2(a), for oxide film thickness larger than 0.5 nm. Therefore, once the interface is formed, the thickness of Si dioxide only increases with further oxidation. Fig. 2(b) shows the areal density of Si⁴⁺ and that of intermediate oxidation states as a function of oxide film thickness. According to this figure, the areal density of Si¹⁺ and that of Si³⁺ repeatedly increase and decrease with a period in thickness of nearly 0.7 nm for thickness less than 1.7 nm. Furthermore, with increasing oxide film thickness, the areal density of Si¹⁺ changes in opposite phase with the areal density of Si³⁺. These findings clearly demonstrate that the interface structure changes periodically with the progress of oxidation for thickness less than 1.7 nm. The decrease in the areal density of Si²⁺

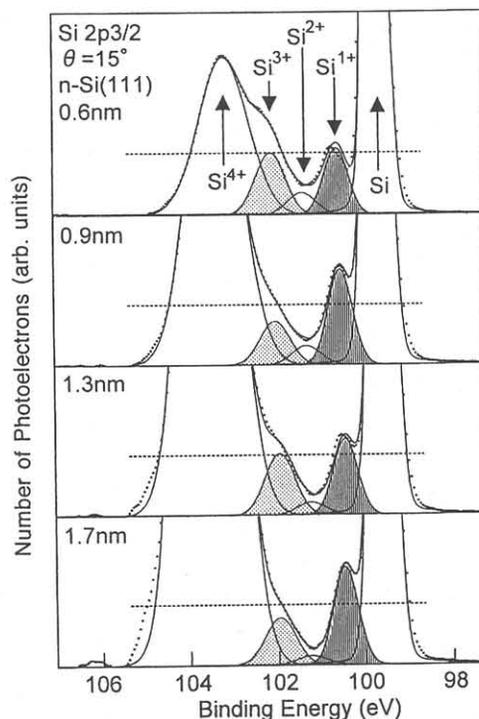


Fig. 1 Oxidation induced changes in Si 2p_{3/2} spectra with oxide film thickness as a parameter.

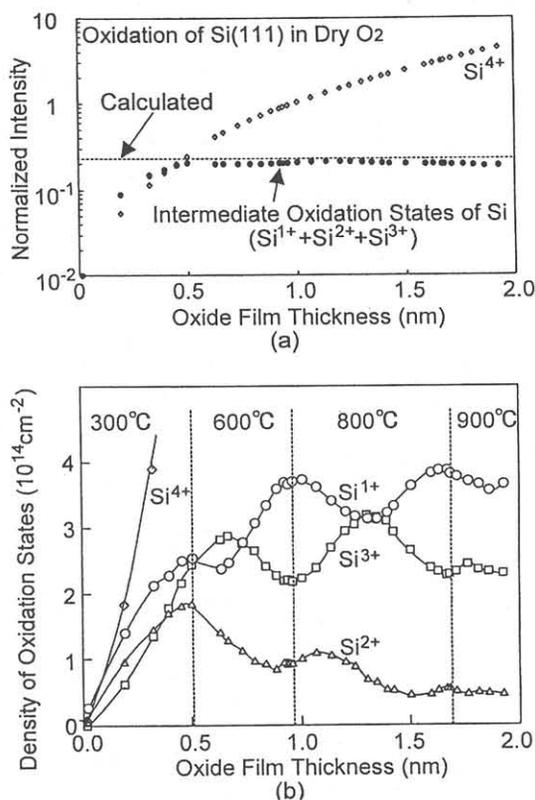


Fig. 2. (a) Dependence of normalized spectral intensity of Si⁴⁺ and summation of intensities of all suboxides on oxide film thickness. (b) Dependence of area densities of Si¹⁺, Si²⁺, Si³⁺, and Si⁴⁺ on oxide film thickness.

with the progress of oxidation in Fig. 2(b) implies that microroughness at the interface decreases with progress of oxidation, because areal density of Si^{2+} must be negligibly small on an atomically flat interface. Fig. 2(b) clearly indicates that oxidation reaction occurs at the interface for oxide thickness range from 0.6 to 1.7 nm.

If the oxidation reaction occurs at the interface, the atomically flat SiO_2/Si interfaces consisting of Si^{1+} and Si^{3+} should appear alternatively. The value of 0.7 nm is obtained for the thickness of two-molecular-layer silicon dioxide by assuming that the oxidation produced volume expansion occurs only along the direction perpendicular to the interface. This calculated value of 0.7 nm is in excellent agreement with the corresponding value of nearly 0.7 nm deduced from Fig. 2(b). For atomically flat interfaces the minimum amounts of Si^{1+} and Si^{3+} must be zero and the amount of Si^{2+} must be close to zero at every stage of oxidation. However, this is not the case. In order to explain the coexistence of Si^{1+} and Si^{3+} in Fig. 2(b), it is necessary to consider the existence of monoatomic atomic steps at every stages of oxidation. However, because the area used for XPS study is on the order of 1 mm^2 , the oxidation reaction observed here must have occurred monolayer by monolayer quite uniformly in atomic scale. Such an oxidation reaction process can be described as a step flow process, in which monoatomic step at the interface moves along the surface with the progress of oxidation.

4. OXIDATION OF H-Si(111)- 2×1 SURFACE

The initial stage of oxidation of H-terminated Si(100)- 2×1 surfaces at 300°C in dry oxygen with a pressure of 1 Torr and subsequent oxidation at 600 and 800°C in the same oxidation atmosphere was studied.¹³⁾ As in the case of H-terminated Si(111)- 1×1 surface, the oxidation proceeds non-uniformly before the formation of one-atomic-layer thick interfacial transition layer. With further oxidation the interface structure deviates extremely from the atomically flat interface, although the abruptness of the interface is preserved. In other words, in this case the layer by layer growth of oxide does not occur.

5. SUMMARY

The non-uniform layer by layer oxidation in atomic scale at the initial stage of oxidation of H-terminated Si(111)- 1×1 surface was found for oxide film thickness of less than 0.5 nm. With further oxidation at 800°C and the oxide was found to grow layer by layer in atomic scale on Si(111) surface. Present results clearly indicates

that even at very small oxide film thickness of less than 1.7 nm the oxidation reaction occurs at the interface. On the other hand, the layer by layer oxidation does not occur on Si(100) surface, even if the preoxide is formed on H-terminated Si(100)- 2×1 surface.

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